

WHAT IS CLAIMED IS:

1. A polymerizable diamantyl monomer having the formula Pg - D -(R)_n, wherein:

5 D is a diamantyl nucleus;

Pg is a polymerizable group covalently bonded to a carbon of the diamantyl nucleus;

n is an integer ranging from 1 to 6, inclusive;

at least one of the R's is a hydrophilic-enhancing moiety; and

10 each of the remaining R's is independently selected from the group consisting of hydrogen and a hydrophilic-enhancing moiety.

2. The diamantyl monomer of claim 1, wherein the hydrophilic-enhancing moiety is selected from the group consisting of a hydroxyl group -OH, a carboxylic group -

15 COOH, an alkyl group -OCH₃ or -OC₂H₅, a keto group -C(O)-, and a group -OC(O)-OCH₃ or -OC(O)-OC₂H₅.

3. The diamantyl monomer of claim 1, wherein the polymerizable group Pg forms a photo-labile polymer.

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4. The diamantyl monomer of claim 1, wherein the polymerizable group Pg is covalently bonded to a tertiary (3°), bridgehead carbon of the diamantyl nucleus.

25 5. The diamantyl monomer of claim 1, wherein the polymerizable group Pg is an unsaturated acid residue bound to the diamantyl nucleus to form an ester.

6. The diamantyl monomer of claim 5, wherein the unsaturated acid residue is an acrylate or a lower alkyl acrylate.

30 7. The diamantyl monomer of claim 6, wherein the unsaturated acid residue is an acrylic acid residue such that the diamantyl monomer is an acrylate monomer.

8. The diamantyl monomer of claim 6, wherein the unsaturated acid residue is a methacrylic acid residue such that the diamantyl monomer is a methacrylate monomer.
9. A polymerizable triamantyl monomer having the formula Pg - D -(R)_n, wherein:
 - 5 D is a triamantyl nucleus;
 - Pg is a polymerizable group covalently bonded to a carbon of the triamantyl nucleus;
 - n is an integer ranging from 1 though 6, inclusive;
 - at least one of the R's is a hydrophilic-enhancing moiety; and
 - 10 each of the remaining R's is independently selected from the group consisting of hydrogen and a hydrophilic-enhancing moiety.
10. The triamantyl monomer of claim 9, wherein the hydrophilic-enhancing moiety is selected from the group consisting of a hydroxyl group -OH, a carboxylic group -COOH, an alkyl group -OCH₃ or -OC₂H₅, a keto group -C(O)-, and a group -OC(O)-OCH₃ or -OC(O)-OC₂H₅.
11. The triamantyl monomer of claim 9, wherein the polymerizable group Pg forms a photo-labile polymer.
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12. The triamantyl monomer of claim 9, wherein the polymerizable group Pg is covalently bonded to a tertiary (3°), bridgehead carbon of the triamantyl nucleus.
13. The triamantyl monomer of claim 9, wherein the polymerizable group Pg is an unsaturated acid residue bound to the triamantyl nucleus to form an ester.
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14. The triamantyl monomer of claim 13, wherein the unsaturated acid residue is an acrylate or a lower alkyl acrylate.
15. The triamantyl monomer of claim 14, wherein the unsaturated acid residue is an acrylic acid residue such that the triamantyl monomer is an acrylate monomer.

16. The triamantyl monomer of claim 14, wherein the unsaturated acid residue is a methacrylic acid residue such that the triamantyl monomer is a methacrylate monomer.

17. A polymerizable, diamondoid-containing monomer having the formula

5 Pg - D -(R)_n, wherein:

D is a diamondoid nucleus selected from the group consisting of tetramantane, pentamantane, hexamantane, heptamantane, octamantane, nonamantane, decamantane, and undecamantane;

10 Pg is a polymerizable group covalently bonded to a carbon of the diamondoid nucleus;

n is an integer ranging from 1 though 6, inclusive;

at least one of the R's is a hydrophilic-enhancing moiety; and

each of the remaining R's is independently selected from the group consisting of hydrogen and a hydrophilic-enhancing moiety.

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18. The diamondoid-containing monomer of claim 17, wherein the hydrophilic-enhancing moiety is selected from the group consisting of a hydroxyl group -OH, a carboxylic group -COOH, an alkyl group -OCH₃ or -OC₂H₅, a keto group -C(O) -, and a group -OC(O)-OCH₃ or -OC(O)-OC₂H₅.

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19. The diamondoid-containing monomer of claim 17, wherein the polymerizable group Pg forms a photo-labile polymer.

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20. The diamondoid-containing monomer of claim 17, wherein the polymerizable group Pg is covalently bonded to a tertiary (3°), bridgehead carbon of the diamondoid nucleus.

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21. The diamondoid-containing monomer of claim 17, wherein the polymerizable group Pg is an unsaturated acid residue bound to the diamondoid nucleus to form an ester.

22. The diamondoid-containing monomer of claim 21, wherein the unsaturated acid residue is an acrylate or a lower alkyl acrylate.

23. The diamondoid-containing monomer of claim 22, wherein the unsaturated acid residue is an acrylic acid residue such that the diamondoid-containing monomer is an acrylate monomer.

24. The diamondoid-containing monomer of claim 22, wherein the unsaturated acid residue is a methacrylic acid residue such that the diamondoid-containing monomer is a methacrylate monomer.

25. A polymer having recurring units selected from the group consisting of:

- a) a diamantyl monomer having a polymerizable group and at least one hydrophilic-enhancing group;
- b) a triamantyl monomer having a polymerizable group and at least one hydrophilic-enhancing group; and
- c) a diamondoid-containing monomer having a polymerizable group and at least one hydrophilic-enhancing group, the diamondoid of the diamondoid-containing monomer selected from the group consisting of tetramantane, pentamantane, hexamantane, heptamantane, octamantane, nonamantane, decamantane, and undecamantane.

26. A deposited layer comprising the polymer of claim 25.

25 27. A method of forming a layer of patterned photoresist on the surface of a substrate, the method comprising the steps of:

- a) forming a polymer from monomers selected from the group consisting of a diamantyl monomer having a polymerizable group and at least one hydrophilic-enhancing group; a triamantyl monomer having a polymerizable group and at least one hydrophilic-enhancing group; and a diamondoid-containing monomer having a polymerizable group and at least one hydrophilic-enhancing group, the diamondoid of the diamondoid-containing monomer selected from the group consisting of tetramantane,

pentamantane, hexamantane, heptamantane, octamantane, nonamantane, decamantane, and undecamantane;

b) depositing the polymer on a surface of the substrate as a polymeric layer, the polymeric layer comprising a photo-labile polymer; and

5 c) exposing selected regions of the polymeric layer to an electromagnetic beam, thereby modifying the photo-labile polymer in those regions exposed to the electromagnetic beam to yield a selectively modified layer.

28. The method of claim 27, additionally comprising the step of contacting the
10 selectively modified layer with a solvent system to solubilize the modified regions.

29. The method of claim 28, wherein the electromagnetic beam comprises radiation having a wavelength less than about 200 nm.

15 30. The method of claim 29, wherein the radiation has a wavelength of about 193 nm.

31. The method of claim 29, wherein the radiation has a wavelength of about 157 nm.

20 32. The method of claim 28, wherein the electromagnetic beam is an e-beam.

33. The method of claim 28 wherein the electromagnetic beam is an x-ray beam.

25 34. A patterned surface formed by the method of claim 27.

35. A method of forming a selected pattern on a surface of a substrate, the method comprising the steps of:

30 a) forming a photo-labile polymer on the surface of the substrate, the photo-labile polymer comprising monomers selected from the group consisting of a diamantyl monomer having at least one polymerizable group and at least one hydrophilic-enhancing group; a triamantyl monomer having a polymerizable group and at least one

hydrophilic-enhancing group; and a diamondoid-containing monomer having a polymerizable group and at least one hydrophilic-enhancing group, the diamondoid of the diamondoid-containing monomer selected from the group consisting of tetramantane, pentamantane, hexamantane, heptamantane, octamantane, nonamantane, decamantane, and undecamantane; and

5 b) exposing selected regions of the layer comprising the photo-labile polymer to an electromagnetic beam, thereby modifying the photo-labile polymer in those regions exposed to the electromagnetic beam to yield a selectively modified layer.

10 36. The method of claim 35, additionally comprising the step of contacting the selectively modified layer with a solvent system to solubilize the modified regions.

37. The method of claim 36, wherein the solvent system comprises an alkali developer solution.

15 38. The method of claim 35, wherein the electromagnetic beam comprises radiation having a wavelength less than about 200 nm.

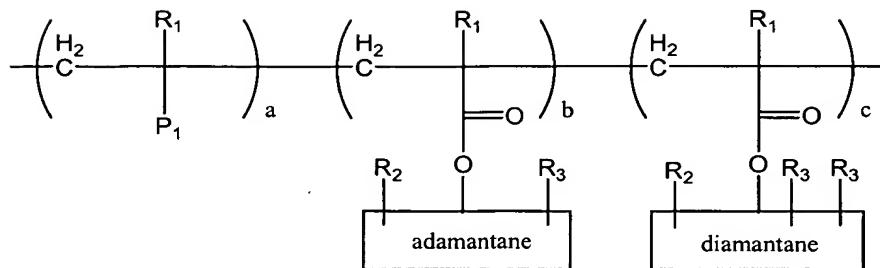
20 39. The method of claim 38, wherein the radiation has a wavelength of about 193 nm.

40. The method of claim 38, wherein the radiation has a wavelength of about 157 nm.

25 41. The method of claim 35, wherein the electromagnetic beam is selected from the group consisting of an e-beam and an x-ray beam.

42. A patterned surface formed the method of claim 35.

30 43. A positive-working photoresist composition comprising a base resin represented by the general formula:



wherein R₁ is selected from the group consisting of -H and -CH₃;

5 R₂ is selected from the group consisting of -H, an alkyl group having from 1 to 4 carbon atoms, and an alkoxy group having from 1 to 4 carbon atoms;

R_3 is $-H$, or a hydrophilic-enhancing moiety selected from the group consisting of a hydroxyl group $-OH$, a keto group $=O$, carboxylic acid group $-COOH$, and alkoxy group $-OR_4$, and a lactone group $-OC(O)OR_4$;

10 R₄ is -CH₃ or -C₂H₅;

a is 0.25 to 0.75;

$$b + c = 1 - a;$$

c is greater than zero; and

P_1 is a non-diamondoid, acid-cleavable pendant group.

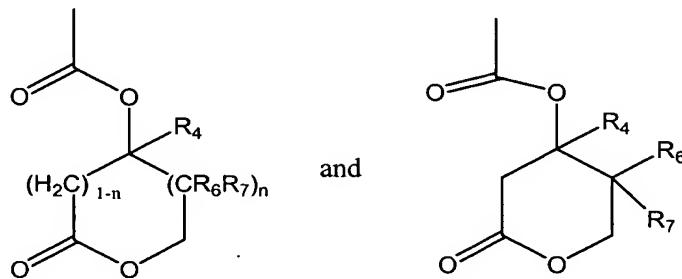
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44. The photoresist composition of claim 43, wherein b is about 0 and c is about 0.5.

45. The photoresist composition of claim 43, wherein P₁ is a lactone-containing pendant group.

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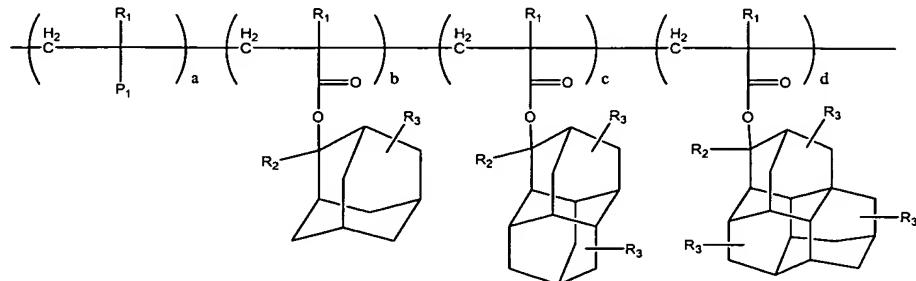
46. The photoresist composition of claim 44, wherein P₁ is selected from the group consisting of:



wherein n is 0 or 1; and

R₄, R₆, and R₇ are each individually selected from the group consisting of H, an alkyl group having from 1 to 4 carbon atoms, and an alkoxy group having from 1 to 4 carbon atoms.

47. A positive-working photoresist composition comprising a base resin represented by the general formula:



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wherein R₁ is selected from the group consisting of -H and -CH₃;

R₂ is selected from the group consisting of -H, an alkyl group having from 1 to 4 carbon atoms, and an alkoxy group having from 1 to 4 carbon atoms;

15 R₃ is -H, or a hydrophilic-enhancing moiety selected from the group consisting of a hydroxyl group -OH, a keto group =O, carboxylic acid group -COOH, and alkoxy group -OR₄, and a lactone group -OC(O)OR₄;

R₄ is -CH₃ or -C₂H₅;

a is 0.25 to 0.75;

20 b + c + d is substantially equal to 1 - a; and

P₁ is a non-diamondoid, acid-cleavable pendant group.

48. The photoresist composition of claim 47, wherein c is about 0 to 0.25.

25 49. The photoresist composition of claim 47, wherein d is about 0 to 0.25.

50. The photoresist composition of claim 47, wherein c + d is about 0 to 0.25.

51. The photoresist composition of claim 47, wherein 3b and 2b are substantially equal to d.

5 52. The photoresist composition of claim 43, wherein P₁ is a lactone-containing pendant group.

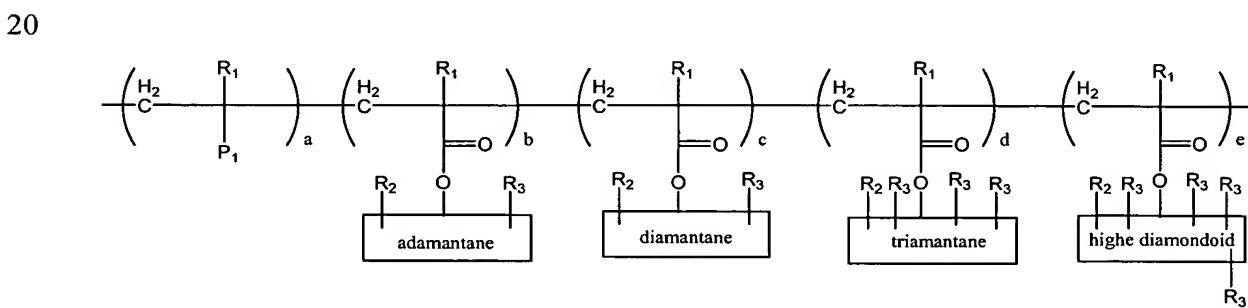
53. The photoresist composition of claim 44, wherein P₁ is selected from the group consisting of:

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wherein n is 0 or 1; and
R₄, R₆, and R₇ are each individually selected from the group consisting of H, an alkyl group having from 1 to 4 carbon atoms, and an alkoxy group having from one to 4 carbon atoms.

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54. A positive-working photoresist composition comprising a base resin represented by the general formula:



wherein R₁ is selected from the group consisting of -H and -CH₃;

R₂ is selected from the group consisting of -H, an alkyl group having from 1 to 4 carbon atoms, and an alkoxy group having from 1 to 4 carbon atoms;

R₃ is -H, or a hydrophilic-enhancing moiety selected from the group consisting of a hydroxyl group -OH, a keto group =O, carboxylic acid group -COOH, and alkoxy group -OR₄, and a group -OC(O)OR₄;

R₄ is -CH₃ or -C₂H₅;

a is 0.25 to 0.75;

b + c + d + e is substantially equal to 1 - a; and

P₁ is a non-diamondoid, acid-cleavable pendant group.

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55. The photoresist composition of claim 54, wherein c ranges from about 0 to 0.25.

56. The photoresist composition of claim 54, wherein d ranges from about 0 to 0.25.

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57. The photoresist composition of claim 54, wherein e ranges from about 0 to 0.25.

58. The photoresist composition of claim 54, wherein c + d + e ranges from about 0 to 0.25.

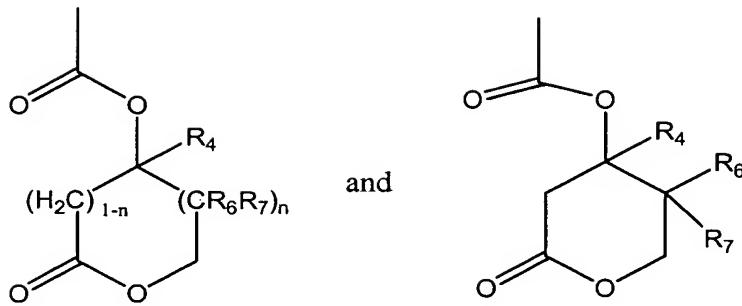
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59. The photoresist composition of claim 54, wherein b, the amount of the adamantane containing monomer, is about equal to c + d + e, the total amount of the diamantane, triamantane, and diamondoid-containing monomers.

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60. The photoresist composition of claim 54, wherein P₁ is a lactone-containing pendant group.

61. The photoresist composition of claim 60, wherein P₁ is selected from the group consisting of:

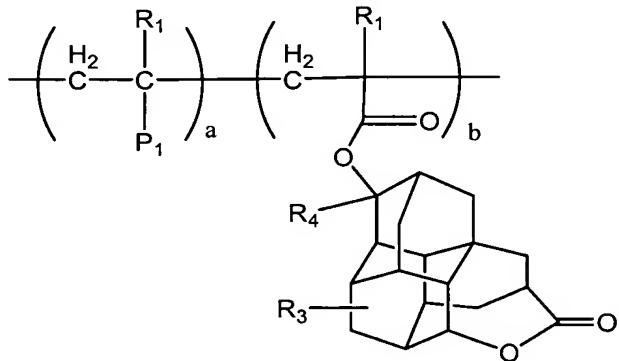


wherein n is 0 or 1; and

5 R_4 , R_6 , and R_7 are each individually selected from the group consisting of H, an alkyl group having from 1 to 4 carbon atoms, and an alkoxy group having from one to 4 carbon atoms.

62. A positive-acting photoresist composition comprising a base resin represented by the general formula:

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wherein R_1 is selected from the group consisting of $-H$ and $-CH_3$;

R_2 is selected from the group consisting of $-H$, an alkyl group having from 1 to 4

15 carbon atoms, and an alkoxy group having from 1 to 4 carbon atoms;

R_3 is $-H$, or a hydrophilic-enhancing moiety selected from the group consisting of a hydroxyl group $-OH$, a keto group $=O$, carboxylic acid group $-COOH$, and alkoxy group $-OR_4$, and a group $-OC(O)OR_4$;

R_4 is $-CH_3$ or $-C_2H_5$;

20 a is 0.25 to 0.75;

$b = 1 - a$; and

P₁ is a non-diamondoid, acid-cleavable pendant group.

63. The photoresist composition of claim 62, wherein b and c each range from about 0 to 0.5.

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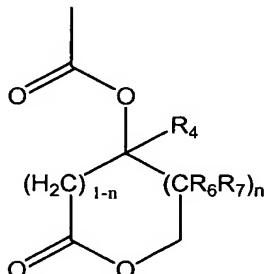
64. The photoresist composition of claim 62, wherein b and c are approximately equal to one another.

65. The photoresist composition of claim 62, wherein P₁ is a lactone-containing

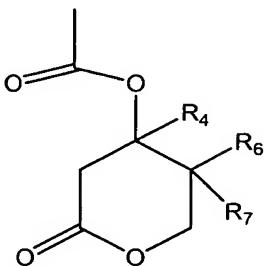
10 pendant group.

66. The photoresist composition of claim 62, wherein P₁ is selected from the group consisting of:

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and

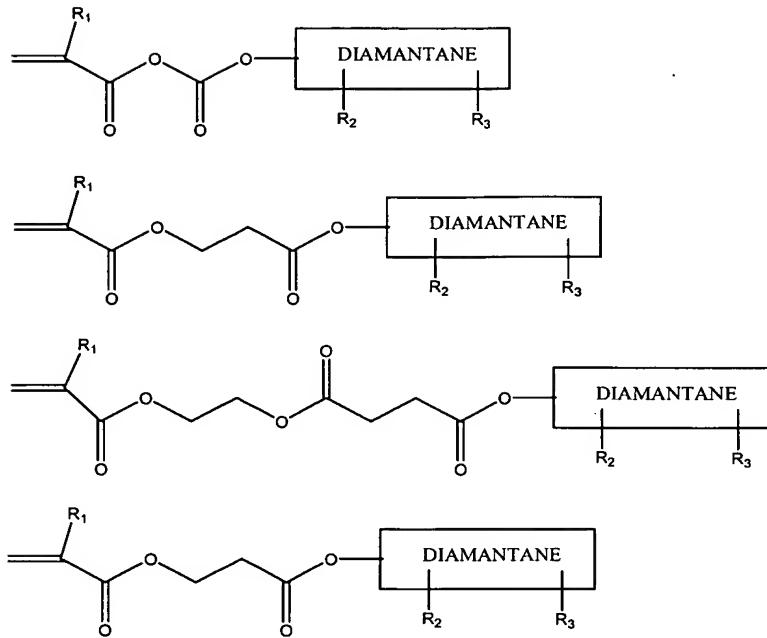


wherein n is 0 or 1; and

R₄, R₆, and R₇ are each individually selected from the group consisting of H, an alkyl group having from 1 to 4 carbon atoms, and an alkoxy group having from 1 to 4 carbon atoms.

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67. A positive-acting photoresist composition comprising a base resin polymerized from any of the following monomers:



wherein R₁ is selected from the group consisting of -H and -CH₃;

R₂ is selected from the group consisting of -H, an alkyl group having from 1 to 4

5 carbon atoms, and an alkoxy group having from 1 to 4 carbon atoms;

R₃ is -H, or a hydrophilic-enhancing moiety selected from the group consisting of a hydroxyl group -OH, a keto group =O, carboxylic acid group -COOH, and alkoxy group -OR₄, and a group -OC(O)OR₄;

R₄ is -CH₃ or -C₂H₅.

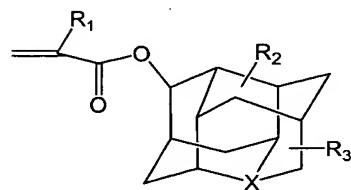
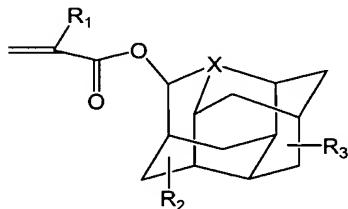
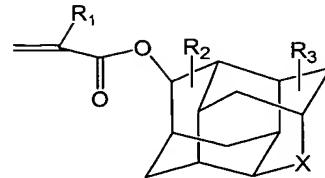
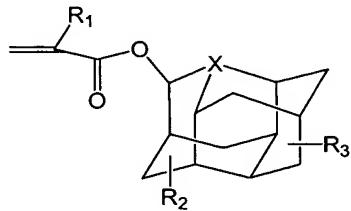
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68. The photoresist composition of claim 67, further including a monomer having adamantanone as a pendant group.

69. The photoresist composition of claim 67, further including a monomer having a
15 diamondoid pendant group.

70. A positive-acting photoresist composition comprising a base resin having a heterodiamondoid as a pendant group.

71. The photoresist composition of claim 70, wherein the base resin is polymerized from any of the following monomers:



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wherein R₁ is selected from the group consisting of -H and -CH₃;

R₂ is selected from the group consisting of -H, an alkyl group having from 1 to 4 carbon atoms, and an alkoxy group having from 1 to 4 carbon atoms;

R₃ is -H, or a hydrophilic-enhancing moiety selected from the group consisting of a hydroxyl group -OH, a keto group =O, carboxylic acid group -COOH, and alkoxy group -OR₄, and a group -OC(O)OR₄;

R₄ is -CH₃ or -C₂H₅;

X is selected from the group consisting of oxygen, nitrogen, boron, and sulfur.

15 72. A positive-acting photoresist composition wherein the base resin comprises

73. The photoresist composition of any of claims 43, 47, 54, 62, 67, or 71, wherein the average Onichi number of any of the diamondoid containing monomers is greater than about 3.

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74. The photoresist composition of any of claims 43, 47, 54, 62, 67, or 71, wherein the average value of the solubility parameter of the base resin, in units of cal^{0.5}/cm^{1.5}, ranges from about 8 to 13.

75. The photoresist composition of any of claims 43, 47, 54, 62, 67, or 71, further including a photoacid generator selected from the group consisting of an onium salt, a diazonium salt, an ammonium salt, a phosphonium salt, an iodonium salt, a sulfonium salt, a selenonium salt, an arsonium salt, an organic halogeno compound, and an organo-
5 metal/organic halide compound.

76. The photoresist composition of claim 75, wherein the photoacid generator has an o-nitorbenzyl type protecting group.

10 77. The photoresist composition of claim 75, wherein the photoacid generator generates a sulfonic acid upon photolysis.

78. The photoresist composition of claim 75, wherein the amount of the photoacid generator in the composition ranges from about 0.01 to 30 weight percent.

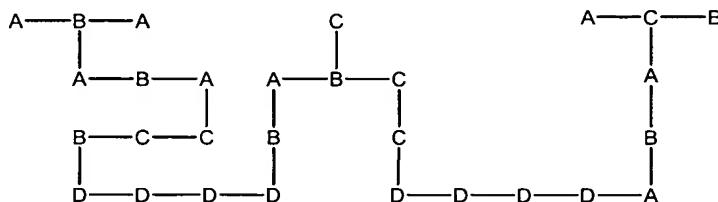
15 79. The photoresist composition of any of claims 43, 47, 54, 62, 67, or 71, wherein the composition further comprises an additive selected from the group consisting of a surface active agent, an organic basic compound, an acid decomposable dissolution inhibiting compound, a dye, a plasticizer, a photosensitizer, a compound promoting
20 solubility in a developing solution, and additives comprising hydrophilic diamondoid derivatives.

25 80. The photoresist composition of any of claims 43, 47, 54, 62, 67, or 71, wherein the composition further includes a solvent selected from the group consisting of ethylene dichloride, cyclohexanone, cyclopentanone, 2-heptanone, γ -butyrolactone, methyl ethyl ketone, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, 2-methoxyethyl acetate, ethylene glycol monoethyl ether acetate, propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), ethylene carbonate, toluene, ethyl acetate, butyl acetate, methyl lactate, ethyl lactate,
30 methyl methoxypropionate, ethyl ethoxypropionate, methyl methoxypropionate, ethyl pyruvate, propyl pyruvate, N,N-dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, and tetrahydrofuran.

81. The photoresist composition of any of claims 43, 47, 54, 62, 67, or 71, wherein the developing solution for the composition includes an aqueous alkaline solution.

82. The photoresist composition of claim 79, wherein the aqueous alkaline solution
5 includes an inorganic alkali such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, aqueous ammonia, a primary amind, ethylamine, n-propylamine, a secondary amine, diethylamine, di-n-butylamine, a tertiary amine, triethylamine, methyldiethylamine, an alcohol amine, dimethylethanamine, triethanolamine, a quaternary ammonium salt, tetramethylammonium hydroxide,
10 tetraethylammonium hydroxide, a cyclic amine, pyrrole, and piperidine.

83. The photoresist composition of any of claims 43, 47, 54, 62, 67, or 71, wherein the base resin comprises a block co-polymer represented by the general formula:



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wherein the D repeat units are lactone containing groups.

84. A method of preparing hydroxylated diamantanes selected from the group
20 consisting of di-hydroxylated diamantane, tri-hydroxylated diamantane, tetra-hydroxylated diamantanes, and mixtures thereof, the method comprising the steps of:

- a) reacting diamantane with N-hydroxyphthalimide (NHPI) and Co(acac)₂ (cobalt (II) acetylacetone) in a reaction mixture;
- b) concentrating the reaction mixture to form a concentrated product; and
- 25 c) recovering hydroxylated diamantanes from the concentrated product.

85. The method of claim 84, further comprising the step of adding additional portions of N-hydroxyphthalimide (NHPI) and Co(acac)₂ (cobalt (II) acetylacetone) to the reaction mixture during step a).

86. The method of claim 84, further comprising the step of dissolving the concentrated product in a solvent, and then extracting the resulting solution with water to form a water layer and a solvent layer.

5 87. The method of claim 86, further comprising the step of subjecting the solvent layer to silica gel column chromatography to recover di-hydroxylated diamantanes.

88. The method of claim 86, wherein the solvent is methylene chloride.

10 89. The method of claim 86, further comprising the steps of dissolving the water layer in ethyl alcohol to form an ethyl alcohol solution, adding activated carbon to the ethyl alcohol solution, and then recovering tri-hydroxylated diamantanes from the activated carbon and ethyl alcohol solution.

15 90. The method of claim 86, further comprising the steps of:

- a) dissolving the water layer in ethyl alcohol to form an ethyl alcohol solution;
- b) adding activated carbon to the ethyl alcohol solution of step a);
- c) concentrating the activated carbon and ethyl alcohol solution of step b) to a concentrated product;
- d) dissolving the concentrated product of step c) in methylene chloride and tetrahydrofuran; and
- e) passing the dissolved concentrated product of step d) through a silica gel column to elute a methylene chloride and tetrahydrofuran fraction and a tetrahydrofuran and ethyl alcohol fraction.

25 91. The method of claim 90, further comprising the step of recovering di-hydroxylated diamantanes from the methylene chloride and tetrahydrofuran fraction.

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92. The method of claim 90, further comprising the step of recovering tri-hydroxylated diamantanes from the tetrahydrofuran and ethyl alcohol fraction.

93. The method of claim 84, further comprising the steps of dissolving the concentrated product in a large excess of methylene chloride to precipitate a solid, and then recovering tetra-hydroxylated diamantane the precipitated solid.

5 94. A method of preparing diamantane methacrylate, the method comprising the step of:

- a) adding methacryloyl chloride to mono-hydroxylated diamantane and triethylamine to form a reaction mixture;
- b) adding an additional amount of methacryloyl chloride and 4-dimethylaminopyridine to the reaction mixture of step a); and
- c) recovering diamantane methacrylate from the reaction mixture of step b).

95. A method of preparing mono-hydroxylated diamantane methacrylate, the method comprising the steps of:

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- a) adding methacryloyl chloride to di-hydroxylated diamantane and triethylamine to form a reaction mixture; and
- b) recovering mono-hydroxylated diamantane methacrylate from the reaction mixture of step a).

20 96. A method of preparing mono-hydroxylated diamantane methacrylate, the method comprising the steps of:

- a) adding methacryloyl chloride to di-hydroxylated diamantane and methacrylic acid to form a reaction mixture;
- b) adding dicyclohexyl carbodiimide and 4-dimethylaminopyridine to the reaction mixture of step a); and
- c) recovering mono-hydroxylated diamantane methacrylate from the reaction mixture of step b).